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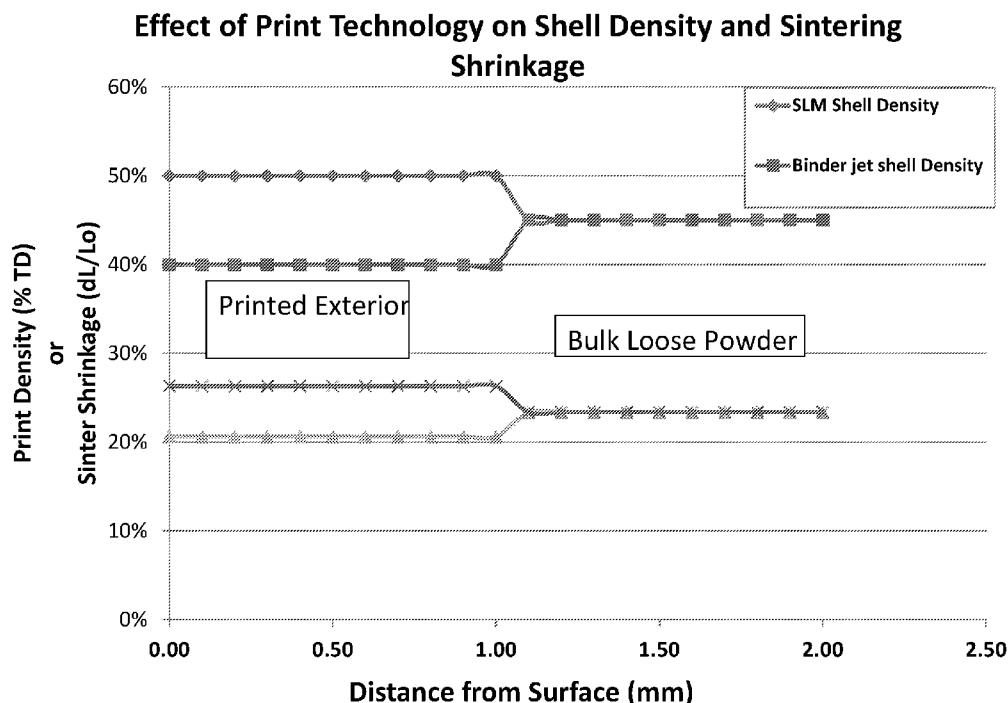


FIG. 1

(57) Abstract: In one aspect, a method of making a sintered article comprises providing a composite article comprising a porous exterior printed from a powder composition via one or more additive manufacturing techniques, the porous exterior defining an interior volume and providing a loose powder component in the interior volume. The porous exterior and loose powder component are simultaneously sintered to provide the sintered article comprising a sintered interior and sintered exterior.

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**ADDITIVE MANUFACTURING TECHNIQUES AND APPLICATIONS THEREOF****RELATED APPLICATION DATA**

The present application claims priority pursuant to Article 8 of the Patent Cooperation  
5 Treaty to United States Provisional Patent Application Serial Number 62/823,149 filed March  
25, 2019 which is incorporated herein by reference in its entirety.

**FIELD**

The present invention relates to additive manufacturing techniques and, in particular, to  
10 additive manufacturing techniques providing enhancements to article density before and after  
sintering.

**BACKGROUND**

Additive manufacturing generally encompasses processes in which digital 3-dimensional  
15 (3D) design data is employed to fabricate an article or component in layers by material  
deposition and processing. Various techniques have been developed falling under the umbrella  
of additive manufacturing. Additive manufacturing offers an efficient and cost-effective  
alternative to traditional article fabrication techniques based on molding processes. With  
additive manufacturing, the significant time and expense of mold and/or die construction and  
20 other tooling can be obviated. Further, additive manufacturing techniques make an efficient use  
of materials by permitting recycling in the process and precluding the requirement of mold  
lubricants and coolant. Most importantly, additive manufacturing enables significant freedom in  
article design. Articles having highly complex shapes can be produced without significant  
expense, allowing the development and evaluation of a series of article designs prior to final  
25 design selection.

However, challenges remain with several additive manufacturing techniques. The binder  
jetting process, for example, requires post-sintering processes to consolidate the printed article to  
a dense finished product. Final density of the product is a result of several variables, including  
green density of the printed article. The green density reflects powder packing efficiency and  
30 contact proximity of adjacent particles. Smaller particles with higher surface area, higher contact  
points and short diffusion distances serve to enhance the densification process during sintering.  
Nevertheless, in powder bed methods, a practical limitation exists of powder size that is both

cost effectively manufactured and easily spread into a continuous layer. Moreover, fine particles tend to cake or agglomerate, thereby developing a lower apparent density. In view of these technical considerations, enhancements are required for improving particle interaction and packing efficiency in additive manufacturing techniques.

5

## SUMMARY

In one aspect, methods of making articles are described herein employing additive manufacturing techniques providing enhancements to article density before and after sintering. Briefly, a method of making a sintered article comprises providing a composite article including  
10 a porous exterior printed from a powder composition via one or more additive manufacturing techniques, the porous exterior defining an interior volume and providing a loose powder component in the interior volume. The porous exterior and loose powder component are simultaneously sintered to provide the sintered article comprising a sintered interior and sintered exterior. In some embodiments, the porous exterior is printed via a powder bed fusion technique  
15 employing radiation or an electron beam to bind particles of the powder composition together. The porous exterior, for example, can have an average density of 50 to 90 percent theoretical density. In another aspect, articles formed according to methods described herein are provided.

These and other embodiments are further described in the following detailed description.

## 20 BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates the printed fractional density and sinter shrinkage difference between a 1 mm porous exterior shell produced by a binder jetting process and a 1 mm porous exterior shell produced by a laser powder bed fusion process. Printed fractional density and sintering shrinkage is measured in a direction proceeding from the porous exterior shell to bulk loose  
25 powder contained within the shell.

## DETAILED DESCRIPTION

Embodiments described herein can be understood more readily by reference to the following detailed description and examples and their previous and following descriptions.  
30 Elements, apparatus and methods described herein, however, are not limited to the specific embodiments presented in the detailed description and examples. It should be recognized that

these embodiments are merely illustrative of the principles of the present invention. Numerous modifications and adaptations will be readily apparent to those of skill in the art without departing from the spirit and scope of the invention.

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#### I. Methods of Making Sintered Articles

In one aspect, a method of making a sintered article comprises providing a composite article comprising a porous exterior printed from a powder composition via one or more additive manufacturing techniques, the porous exterior defining an interior volume, and providing a loose powder component in the interior volume. The porous exterior and loose powder component are simultaneously sintered to provide the sintered article comprising a sintered interior and sintered exterior.

Turning now to specific steps, the porous exterior is printed from a powder composition via one or more additive manufacturing techniques. In some embodiments, the porous exterior is printed via a powder bed fusion technique employing radiation or an electron beam to bind particles of the powder composition together. The porous exterior, for example, can be printed via selective laser melting (SLM), selective laser sintering (SLS), or electron beam melting (EBM). Density of the porous exterior can be selected according to various considerations including, but not limited to, design features and/or size of the composite article, strength requirements for handling the composite article in subsequent operations including sintering, thickness of the exterior, and/or density of the loose powder component in the interior volume. The porous exterior can generally have an average density of 50-90 percent theoretical density. In some embodiments, the porous exterior has an average density ranging from 60-85 percent or from 65-80 percent theoretical density. In some embodiments, density of the composite article exterior is uniform or substantially uniform. In being substantially uniform, density of exterior varies less than 10 percent or less than 5 percent from location to location.

Alternatively, the composite article exterior can comprise one or more density or porosity gradients. In some embodiments, the porous exterior can exhibit a sintering gradient along the exterior thickness. The porous exterior may exhibit less sintering and lower density adjacent to the loose powder component. Sintered density may increase in the porous exterior in a direction moving away from the interior volume. In such embodiments, the green density of the loose

powder component and sintered exterior can be more closely matched, thereby reducing cracking and other stresses that can compromise structural integrity of the sintered article.

Structural features of the exterior may also exhibit differing densities. Density gradients of the exterior can have various functions, such as reinforcing areas of the composite article experiencing downstream handling forces, controlling residual stress from sintering shrinkage, accommodating sintering distortions due to tray friction and/or gravitational effects, and creating compressive stresses in the composite article and/or sintered article.

Porosity of the composite article exterior can be interconnected, in some embodiments. In this way, gases are permitted to escape the interior of the composite article during subsequent sintering and/or heat treatment operations. Pore size of the composite exterior can be generally uniform or can vary. Pore size can also be sufficiently small to preclude the loose powder component from passing through the porous exterior.

In some embodiments, the porous exterior forms less than 60 volume percent of the composite article. Volume percent of the composite article formed by the porous exterior can also have a value selected from Table I.

Table I – Composite Article vol.% formed by Porous Exterior

|       |
|-------|
| ≤ 50  |
| ≤ 40  |
| ≤ 30  |
| ≤ 25  |
| ≤ 20  |
| ≤ 15  |
| ≤ 10  |
| 5-50  |
| 5-40  |
| 5-30  |
| 5-20  |
| 10-30 |
| 10-20 |

As described herein, the porous exterior defines an interior volume comprising a loose powder component. In being in the loose state, the powder component is free-flowing and is not restricted. The porous exterior can serve as one or more walls defining an interior of the composite article in which the loose powder component is positioned. Arrangement of exterior walls defining the interior volume is dependent on design parameters specific to the article. For

example, if the composite article is a hollow cylinder, a porous inner diameter (ID) wall and porous outer diameter (OD) wall can be formed via one or more additive manufacturing techniques. The porous ID and OD walls define a volume between the walls comprising a loose powder component.

5           The loose powder component and the powder composition of the porous exterior can have the same or substantially the same composition, in some embodiments. Alternatively, the loose powder component and the powder composition of the porous exterior are of differing compositions. The loose powder component and powder composition of the porous exterior can be independently selected from the group consisting of powder metal and powder alloy. Powder  
10   metal can comprise aluminum or any transition metal including, but not limited to, metals of Groups IVB-VIIIB of the Periodic Table. Powder metal can also comprise a transition metal selected from Groups IB and IIB of the Periodic Table. Groups of the Periodic Table described herein are identified according to the CAS designation.

          Powder alloy of the porous exterior and/or loose powder component, in some  
15   embodiments, comprises cobalt-based alloy, nickel-based alloy or iron-based alloy. Cobalt-based powder alloy is commercially available under the STELLITE®, HAYNES®, and/or TRIBALLOY® trade designations. Moreover, nickel-based powder alloy is commercially available under the INCONEL®, HASTELLOY® and/or BALCO® trade designations for some embodiments. Additionally, powder alloy can comprise unweldable superalloys.

20           Alternatively, the loose powder component and/or powder composition of the porous exterior comprises metal carbide grains. In some embodiments, for example, metal carbide grains comprise tungsten carbide. Metal carbide grains can also include carbides of one or more of niobium, vanadium, tantalum, chromium, zirconium and/or hafnium in addition to tungsten carbide. In other embodiments, the loose powder component and/or powder composition of the  
25   porous exterior comprises ceramic particles. Any ceramic particles consistent with the objectives described herein can be used. Suitable ceramics, in some embodiments, comprise metal nitrides, metal carbonitrides, metal carboxynitrides, metal oxides, and/or metal borides.

          In some embodiments, metal carbide of the loose powder component and/or exterior powder composition are sintered cemented carbide particles. As detailed further herein, an  
30   individual sintered cemented carbide particle comprises multiple metal carbide grains sintered together in conjunction with metallic binder. In the loose condition, the sintered cemented

carbide particles can have apparent density of at least 4 g/cm<sup>3</sup>, in some embodiments. As known to one of skill in the art, apparent density is the mass of a unit volume of powder or particles in the loose condition, usually expressed in g/cm<sup>3</sup>. In some embodiments, sintered cemented carbide particles have apparent density of at least 7 g/cm<sup>3</sup>. Apparent density of sintered cemented carbide particles of grade powders described herein can also have values selected from Table II.

Table II – Apparent Density of Sintered Cemented Carbide Particles

|                         |
|-------------------------|
| > 4 g/cm <sup>3</sup>   |
| > 5 g/cm <sup>3</sup>   |
| ≥ 6.5 g/cm <sup>3</sup> |
| ≥ 7.5 g/cm <sup>3</sup> |
| ≥ 8 g/cm <sup>3</sup>   |
| ≥ 9 g/cm <sup>3</sup>   |
| 6-11 g/cm <sup>3</sup>  |
| 7-11 g/cm <sup>3</sup>  |
| 8-11 g/cm <sup>3</sup>  |

Apparent density of sintered cemented carbide particles of grade powders can also be less than 6 g/cm<sup>3</sup>. For example, apparent density of sintered cemented carbide particles can range from 2-6 g/cm<sup>3</sup>, in some embodiments. Apparent density of sintered cemented particles can be determined according to ASTM B212 Standard Test Method for Apparent Density of Free-Flowing Metal Powders using the Hall Flowmeter Funnel.

In addition to apparent density, sintered cemented carbide particles employed in the composite article can have tap density of at least 5 g/cm<sup>3</sup>. In some embodiments, sintered cemented carbide particles exhibit tap density having a value selected from Table III.

Table III – Tap Density of Sintered Cemented Carbide Particles

|                         |
|-------------------------|
| ≥ 6 g/cm <sup>3</sup>   |
| ≥ 7 g/cm <sup>3</sup>   |
| ≥ 7.5 g/cm <sup>3</sup> |
| ≥ 8 g/cm <sup>3</sup>   |
| ≥ 8.5 g/cm <sup>3</sup> |
| ≥ 9.5 g/cm <sup>3</sup> |
| 7-12 g/cm <sup>3</sup>  |
| 8-12 g/cm <sup>3</sup>  |
| 9-12 g/cm <sup>3</sup>  |

Tap density of sintered cemented carbide particles, powder metal and/or powder alloy can be determined according to ASTM B527 Standard Test Method for Tap Density of Metal Powders and Compounds. In some embodiments, the ratio of tap density to apparent density (Hausner ratio) of sintered cemented carbide particles is 1.05 to 1.50. Hausner ratio of sintered cemented carbide particles, in some embodiments is 1.1 to less than 1.50.

In addition to apparent density and tap density, sintered cemented carbide particles can have an average individual particle density of at least 80 percent theoretical density. In some embodiments, average individual particle density of the sintered cemented carbide particles is at least 90 percent or at least 95 percent theoretical density. Sintered cemented carbide particles can exhibit an average individual particle density of 80 to 95 percent theoretical density, in some embodiments. In further embodiments, sintered cemented carbide particles can exhibit an average individual particle density of 90 to 98 percent theoretical density.

As described further herein, the foregoing apparent densities, tap densities and individual particle densities can be achieved through one or several sintering processes administered during formation of the particles. The sintering processes, in some embodiments, do not employ sintering inhibitor(s) to mitigate particle sticking or adhesion. Sintered cemented carbide particle properties described herein can be achieved in the absence of sintering inhibitor(s). In some embodiments, sintered cemented carbide particles are prepared by sintering a grade powder at temperatures of 1100°C to 1400°C for 0.5 to 2 hours to provide a sintered compact. The sintered compact is subsequently milled to provide individual sintered cemented carbide particles. Depending on particle morphology and density, the sintered cemented carbide particles can be further heat treated for further densification. Further heat treatment can include plasma densification, such as plasma spheroidization using an RF plasma torch or DC plasma torch. Alternatively, the sintered cemented carbide particles can be re-sintered forming a second compact. The second compact is milled to provide the sintered cemented carbide particles. Further densification treatments can be administered any desired number of times to provide sintered cemented carbide particles desired apparent densities, tap densities and/or individual particle densities. Sintering times and temperatures can be selected according to several considerations including, but not limited to, binder content of the cemented carbide particles, desired sintered particle density and sintering stage. In some embodiments, early sintering stages are conducted at lower temperatures and/or shorter times to facilitate milling the sintered

compact. For example, an initial or early stage sintering process may be administered at temperatures below binder liquefaction. Late stage or final sintering processes may achieve higher temperatures, such as temperatures at which liquid phase sintering takes place.

Alternatively, sintered cemented carbide particles have been developed for unrelated applications, such as thermal spray and other cladding applications. In some embodiments, sintered cemented carbide particles commercially available for these unrelated applications may be employed in the loose powder component and/or composite article exterior described herein. Sintered cemented carbide particles developed for thermal spray/cladding applications, for example, are commercially available from Global Tungsten and Powders Corporation under the Powder Perfect trade designation.

Sintered cemented carbide particles can generally have an average size of 1  $\mu\text{m}$  to 100  $\mu\text{m}$ . In some embodiments, sintered cemented carbide particles have an average size selected from Table IV.

Table IV – Average Sintered Cemented Carbide Particle Size ( $\mu\text{m}$ )

|       |
|-------|
| 5-90  |
| 5-50  |
| 10-75 |
| 10-50 |
| 5-40  |
| 20-40 |
| 0.5-2 |
| 1-5   |
| 1-10  |

Sintered cemented carbide particles can exhibit a Gaussian particle size distribution, in some embodiments. In other embodiments, sintered cemented carbide particles can have a polydisperse, bimodal or multi-modal particle size distribution. In further embodiments, sintered cemented carbide particles can be monodisperse or substantially monodisperse. In being substantially monodisperse, the cemented carbide particles are within  $\pm 10$  percent or  $\pm 5$  of the average particle size. In some embodiments, sintered cemented carbide particles are spherical or substantially spherical in shape. Alternatively, sintered cemented carbide particles can be a mixture of irregularly shaped particles with spherical or substantially spherical particles.

Sintered cemented carbide particles comprise one or more metal carbides selected from the group consisting of Group IVB metal carbides, Group VB metal carbides and Group VIB metal carbides. In some embodiments, tungsten carbide is the sole metal carbide of the sintered particles. In other embodiments, one or more Group IVB, Group VB and/or Group VIB metal carbides are combined with tungsten carbide to provide individual sintered particles. For example, chromium carbide, titanium carbide, vanadium carbide, tantalum carbide, niobium carbide, zirconium carbide and/or hafnium carbide and/or solid solutions thereof can be combined with tungsten carbide in sintered particle production. Tungsten carbide can generally be present in the sintered particles in an amount of at least about 80 or 85 weight percent. In some embodiments, Group IVB, VB and/or VIB metal carbides other than tungsten carbide are present in the sintered particles in an amount of 0.1 to 5 weight percent.

Sintered cemented carbide particles comprise metallic binder. Metallic binder of sintered cemented carbide particles can be selected from the group consisting of cobalt, nickel and iron and alloys thereof. In some embodiments, metallic binder is present in the sintered cemented carbide particles in an amount of 0.1 to 35 weight percent. Metallic binder can also be present in the sintered cemented carbide particles in an amount selected from Table V.

Table V – Metallic Binder Content (wt.%)

|        |
|--------|
| 0.1-20 |
| 0.1-10 |
| 0.5-15 |
| 1-10   |
| 3-20   |
| 5-15   |
| 12-15  |
| 10-35  |
| 15-35  |
| 15-25  |

Metallic binder of the sintered cemented carbide particles can also comprise one or more additives, such as noble metal additives. In some embodiments, the metallic binder can comprise an additive selected from the group consisting of platinum, palladium, rhenium, rhodium and ruthenium and alloys thereof. In other embodiments, an additive to the metallic binder can comprise molybdenum, silicon or combinations thereof. Additive can be present in the metallic binder in any amount not inconsistent with the objectives of the present invention. For example,

additive(s) can be present in the metallic binder in an amount of 0.1 to 10 weight percent of the sintered cemented carbide particles.

As detailed further herein, portions of the composite article formed by additive manufacturing are largely limited to the porous exterior, wherein the loose powder component of the interior completes the remainder of the composite article. In this way, the loose powder component forms the bulk of the composite article and is spatially free to pack in the most efficient manner. In some embodiments, the loose powder component can be vibrated and/or subjected to mechanical agitation to further enhance packing characteristics and higher green densities. In contrast, the powder composition of the printed exterior exhibits limited freedom of movement due to partial sintering. Accordingly, the exterior exhibits pores and/or other powder packing inefficiencies. As a result of these packing inefficiencies, volume of the composite article occupied by the porous exterior can be minimized. In some embodiments, the porous exterior is limited to a volume percent selected from Table I above. Moreover, the porous exterior can generally exhibit thickness of less than 1.5 mm. Thickness of the porous exterior can be dependent on several considerations including, but not limited to, porosity or density of the porous exterior, overall size of the sintered article, and/or mass of the loose powder component in the interior volume defined by the porous exterior.

The interior volume defined by the porous exterior can have any desired dimensions. Dimensions of the interior volume can be selected according to the particular design of the composite article. In some embodiments, the interior volume has at least one dimension greater than 0.5 mm. In some embodiments, one or more dimensions of the interior volume have a value selected from Table VI.

Table VI – Interior Volume Dimension (mm)

|             |
|-------------|
| $\geq 0.75$ |
| $\geq 1$    |
| $\geq 5$    |
| 0.5-1000    |
| 1-1000      |
| 5-5000      |

The interior volume can have any desired shape, including polygonal, spherical, elliptical and any combination of straight and curved surfaces.

As illustrated in FIG. 1, the porous exterior or shell formed by a laser powder bed fusion technique exhibits higher density than the bulk density of the loose powder component, leading to a higher density of the composite article. The opposite is true for the porous exterior formed by a binder jetting process. The binder jetted porous exterior or shell exhibits lower density  
5 relative to the bulk density of the loose powder component. In view of this difference, the porous exterior formed via the laser powder bed fusion experiences less sintering shrinkage than the binder jetted exterior, thereby reducing the potential for cracking and/or other structural defects during sintering of the composite article to provide the sintered article. Porous exteriors formed by laser powder bed or electron beam powder bed fusion techniques described herein  
10 provide additional advantages of enabling articles of larger dimensions, reducing the volume of the porous exterior, reducing fabrication time of the articles, eliminating the need for structures to support the articles during fabrication and their post-processing removal, and/or eliminating potential contamination effects associated with binder jetted parts.

In some embodiments, the porous exterior is formed around the loose powder component  
15 by one or more additive manufacturing techniques described herein. Formation of the exterior around the loose powder component can enable complete production of the composite article at the conclusion of the additive manufacturing process. Strength of the composite article can also be enhanced via one or more printed infill structures residing in the interior volume defined by the porous exterior. Infill structures can have any design consistent with enhancing strength of  
20 the composite article. In some embodiments, one or more lattice structures span the interior volume. Specific design and placement of infill structures can be dependent on particular design parameters and strength requirements of the composite article. Infill structures can be uniform or substantially uniform in design and/or placement in the interior volume, in some embodiments. In other embodiments, infill structures can vary in design and/or placement in the interior  
25 volume. For example, size of the interior volume may vary over the article requiring variable sizes of infill structural elements. In some embodiments, infill structures can provide sufficient strength to the composite article to permit the porous exterior to match or substantially match density of the interior powder component. Infill structures may also assist in preventing significant shifting or densifying of loose powder, thereby reducing the potential for separation  
30 of the porous exterior from the loose powder component during sintering of the composite article.

Infill structures can also exhibit one or more functionalities unrelated to enhancing strength of the composite article. Infill structures, for example, can be one or more conduits of various cross-sectional geometry and/or diameter. One or more conduits in the interior can serve as fluid flow channels in the final sintered article. Fluid flow channels can be employed as flow channels for coolant, including cryogenic coolant. The coolant can be used to cool the sintered article during use of the article in one or more applications, including tooling applications. The coolant can also be transferred to one or more articles downstream of the sintered article.

Infill structures can assist in reducing exterior wall thickness and the volume occupied by the porous exterior. Dimensions of the infill structures, including lattice structures, can be selected such that the structures blend into the sintered interior and are, therefore, not discernable from the remainder of the sintered interior formed by the loose powder component. In other embodiments, infill structure(s) remain discernable in the sintered interior of the sintered article. Infill structures can be formed by the additive manufacturing techniques employed in fabrication of the porous exterior.

In some embodiments, the porous exterior is formed by the additive manufacturing process, and the loose powder component is subsequently added to the interior volume defined by the exterior. Once formed, the composite article is subjected to one or more sintering processes to provide the sintered article. The porous exterior and loose powder component are simultaneously sintered or co-sintered, thereby forming a sintered interior and sintered exterior of the article. Sintering times and temperatures can be selected according to several considerations including, but not limited to, compositional identity of the exterior and loose powder component, dimensions of the composite article and desired strength of the sintered article. In some embodiments, the sintered article can be subjected to hot isostatic pressing (HIP). HIP can be administered during or subsequent to the sintering process. Alternatively, desired density of the sintered article can be achieved without a HIP cycle.

The sintered interior and sintered exterior of the article can be continuous with one another. Moreover, a density gradient can exist between the sintered interior and sintered exterior. The sintered interior can exhibit a higher density than the sintered exterior. Alternatively, the sintered exterior can exhibit a higher density than the sintered interior. Methods described herein can further comprise grinding or mechanically removing at least a

portion of the sintered exterior. The sintered exterior, in some embodiments, is completely removed from the sintered article leaving behind the sintered interior.

Methods described herein provide additional technical enhancements and advantages. Higher densities of composite articles can lower sintering temperature and obviate the need for  
5 HIP cycles to produce article of high density via additive manufacturing techniques. Lower sintering temperatures can inhibit grain growth and provide fine grain sintered articles exhibiting high hardness and high wear resistance.

Moreover, elimination of the binder by employing laser powder bed fusion or electron  
10 beam powder bed fusion to form the porous exterior of the composite article can reduce or preclude defects, such as cracking and pore formation, due to gas expansion and gas pocket formation during thermal debinding. This has the added technical effect of enabling thicker articles not previously realized due to internal cracking and voids formed during debinding and/or sintering.

Various embodiments of the invention have been described in fulfillment of the various  
15 objects of the invention. It should be recognized that these embodiments are merely illustrative of the principles of the present invention. Numerous modifications and adaptations thereof will be readily apparent to those skilled in the art without departing from the spirit and scope of the invention.

CLAIMS

1. A method of making a sintered article comprising:  
providing a composite article including a porous exterior printed from a powder  
composition via one or more additive manufacturing techniques employing powder bed fusion  
5 with radiation, the porous exterior defining an interior volume;  
providing a loose powder component in the interior volume; and  
simultaneously sintering the porous exterior and loose powder component to provide the  
sintered article comprising a sintered interior and sintered exterior.
- 10 2. The method of claim 1, wherein the powder bed fusion technique is selective laser  
sintering or selective laser melting.
3. The method of claim 1, wherein the additive manufacturing technique comprises electron  
beam melting.
- 15 4. The method of claim 1, wherein the porous exterior has an average density of 50 to 90  
percent theoretical density.
5. The method of claim 1, wherein the porous exterior has an average density of 60 to 85  
20 percent theoretical density.
6. The method of claim 1, wherein the porous exterior comprises one or more density  
gradients.
- 25 7. The method of claim 1, wherein average density of the sintered article is at least 97  
percent theoretical density.
8. The method of claim 1 comprising a density gradient between the sintered interior and  
sintered exterior.

30

9. The method of claim 1, wherein the powder composition of the porous exterior and the loose powder component have the same composition.

10. The method of claim 1, wherein the powder composition of the porous exterior and the loose powder component are of differing compositions.

11. The method of claim 1, wherein the powder composition of the porous exterior and the loose powder component are independently selected from the group consisting of powder metal and powder alloy.

12. The method of claim 11, wherein the powder metal and powder alloy are unweldable.

13. The method of claim 1, wherein the powder composition of the porous exterior and the loose powder component comprise one or more ceramic materials.

14. The method of claim 1, wherein the powder composition of the porous exterior and the loose powder component comprise sintered cemented carbide particles.

15. The method of claim 14, wherein the sintered cemented carbide particles have apparent density of 6-11 g/cm<sup>3</sup>.

16. The method of claim 1, wherein the porous exterior has thickness less than or equal to 0.5 mm.

17. The method of claim 1, wherein the porous exterior is formed around the loose powder component.

18. The method of claim 1, wherein the loose powder component is added to the interior volume.

19. The method of claim 1 further comprising printing one or more lattice structures in the interior volume.

20. The method of claim 19, wherein the lattice structures span the interior volume,  
5 contacting sections of the porous exterior.

21. The method of claim 19, wherein the loose powder component surrounds the lattice structures.

10 22. The method of claim 1 further comprising printing one or more conduits in the interior volume.

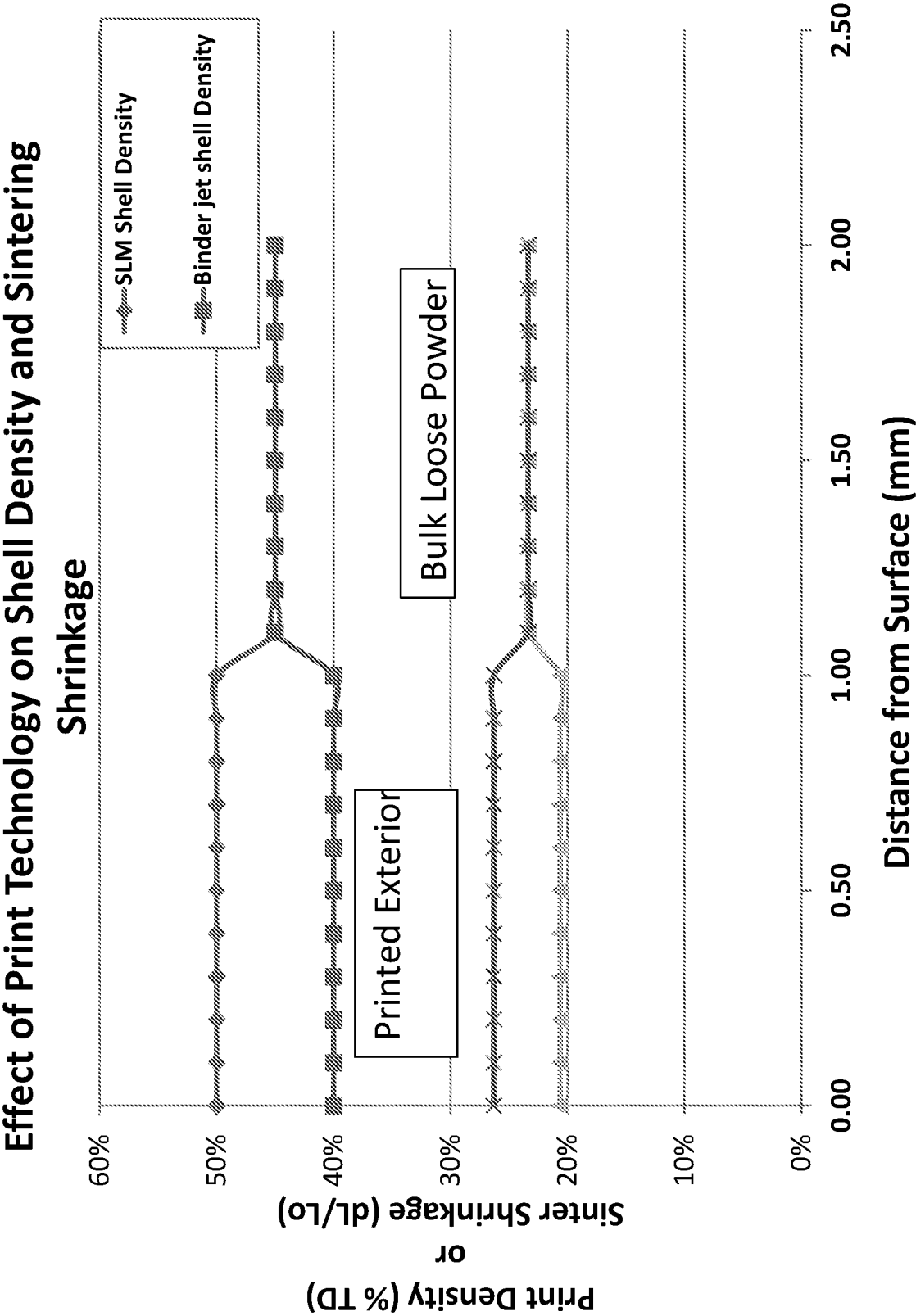


FIG. 1

**A. CLASSIFICATION OF SUBJECT MATTER****B22F 3/105(2006.01)i, B33Y 10/00(2015.01)i, B33Y 50/02(2015.01)i, B33Y 70/00(2015.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

B22F 3/105; B21H 1/12; B21K 1/04; B22F 1/02; B22F 3/00; B22F 3/15; B22F 5/00; B22F 7/06; B28B 1/52; C04B 35/80; B33Y 10/00; B33Y 50/02; B33Y 70/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) &amp; Keywords: additive manufacturing, porous, loose powder, sintering, exterior

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                           | Relevant to claim No. |
|-----------|--------------------------------------------------------------------------------------------------------------|-----------------------|
| A         | WO 2016-094704 A1 (MATERION CORPORATION) 16 June 2016<br>paragraphs [0031]–[0049]                            | 1–22                  |
| A         | US 2017-0369382 A1 (SAFRAN AIRCRAFT ENGINES et al.) 28 December 2017<br>paragraphs [0088]–[0091]             | 1–22                  |
| A         | US 2015-0283614 A1 (GENERAL ELECTRIC COMPANY) 08 October 2015<br>paragraphs [0037]–[0042]; and figures 3A–3F | 1–22                  |
| A         | US 4059879 A (CHMURA et al.) 29 November 1977<br>claims 1–5                                                  | 1–22                  |
| PX        | US 2019-0168299 A1 (KENNAMETAL INC.) 06 June 2019<br>paragraphs [0011]–[0028]; and claims 1–11               | 1–22                  |



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents:

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"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

14 July 2020 (14.07.2020)

Date of mailing of the international search report

**14 July 2020 (14.07.2020)**

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/US2020/024495**

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s)                                                                                                                                                                         | Publication<br>date                                                                                                                                    |
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| US 2019-0168299 A1                        | 06/06/2019          | CN 109865838 A<br>DE 102018128370 A1                                                                                                                                                               | 11/06/2019<br>06/06/2019                                                                                                                               |